

Research article

The competition between self-seeding and specific nucleation in crystallization of long-chain branched polypropylene

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Abstract. The main purpose of this work is to present the effect of long-chain branching and specific α -nucleation on the optical properties, crystallization and supermolecular structure of polypropylene (PP). Commercially available α -nucleating/clarifying agent 1,3;2,4-bis(3,4-dimethylbenzylidene)sorbitol (Millad 3988) was mixed into linear PP and long-chain branched PP (LCB-PP) in the concentration of 0.2 wt%. For the study of polymorphic composition, crystallinity, and crystallization process under isothermal conditions in the temperature range of 130–150 °C, differential scanning calorimetry and wide-angle X-ray scattering were used. Although the used nucleating/clarifying agent appears to have a slight effect on the optical properties of long-chain branched polypropylene, it does not appear to affect the crystallization kinetics significantly. LCB-PP exhibited self-nucleation, favored over nucleation by a specific nucleating agent.

Keywords: polyolefins, crystallization, crystal structure, morphology, differential scanning calorimetry, X-ray, nucleating agent

1. Introduction

Isotactic polypropylene (PP) is one of the most essential semi-crystalline polymers of modern times due to its wide range of applications, suitable mechanical properties and low price. Polypropylene is characterized by low density, relatively high melting point and good chemical resistance. Commercial PP is commonly prepared using iso-specific Ziegler-Natta or metallocene catalysts. This type of preparation produces highly linear chains and narrow molecular weight distribution, resulting in low melt strength and no strain hardening, which limits its processing by thermoforming, coating, foaming, or film-blowing [1, 2]. An effective method for improving these limiting properties is the introduction of long chains on the polypropylene backbone [3–6].

Two main methods are used to prepare the long-chain branched polypropylene (LCB-PP). The post-reactor method is based on the disruption of the main chain of PP and subsequent grafting of long branches onto the main chain of the polymer by chemical grafting reaction in the molten state, for example, in the presence of peroxides [7–9] or by high-energy irradiation in solid state [10, 11]. Long-chain branching can also be achieved in situ during polypropylene polymerization by adding a suitable comonomer [12, 13]. Polypropylene exhibits a polymorphic structure with well-defined distinct α -, β -, γ - and smectic phases, the last formed during high undercooling [14]. Monoclinic α -phase, developed during ordinary processing conditions, forms two variants; α_1 with random down-up directions of methyl groups and more stable α_2

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with ordered methyl groups [15]. β -phase can be obtained by creating favorable crystallization conditions, such as a high-temperature gradient, the presence of shear forces, or by using heterogeneous β -nucleating agents, resulting in a trigonal lattice. Compared to the α -phase, it exhibits much better toughness and ductility but is thermodynamically less stable. β -phase can recrystallize into the α -phase upon stretching at high temperatures [16–19]. The third crystalline phase of polypropylene is the orthorhombic γ -phase which rarely occurs under particular thermodynamic conditions, either by the action of very high pressure or by using samples with a low molecular weight [20].

The change of the PP molecular architecture, by introducing long-chain branching, strongly influences the process of crystallization and resulting morphology. LCB-PP contains structural defects, which affect both the nucleation and growth of crystallites. In the case of LCB-PP produced by a radical-driven synthesis process using peroxides in the melt state, not only are long branches created, but the process is also accompanied by chain scission and gel formation, which can strongly affect the nucleation rate. The self-seeding effect of LCB-PP has already been observed [21–23]. The presence of defects in the form of branching points, on the other hand, reduces the rate of crystallite growth. However, the overall crystallization is faster in the case of LCB-PP. [4, 22] As for polymorphic composition, the presence of long branches and thus a higher amount of irregularities on the polymer backbone causes a higher ability of PP to crystallize into the orthorhombic γ -phase side by side to α -phase [24], even at elevated pressures [3]. At the same time, the crystallization temperature itself has a non-negligible effect, which affects the helical conformation regularity. It, therefore, strongly influences the resulting crystalline phase structure of LCB-PP [1].

Nucleating agents are often used in PP to shorten processing cycles and to modify final properties, mainly mechanical and optical properties. For the improvement of the optical properties, so-called clarifying agents are used, which nucleate into the α -phase and significantly reduce the size of the crystallites, resulting in less light scattering [25–27]. Due to the polymorphism of PP, several nucleating agents are also used to cause crystallization into the β -phase. The effectiveness of a commercial β -nucleating agent in LCB-PP and mixtures of LCB-PP with

linear PP was investigated in the work of Gajzlerova et al. [22]. It was found that the self-nucleation effect of LCB-PP is dominant, and the formation of β -phase is suppressed [22, 28–31].

The process of nucleation of PP by the sorbitol-based clarifying α -nucleating agent is well documented and widely studied [32–36]; however, LCB-PP has not been appropriately investigated in this context yet. Thus, this work analyzes the effect of a sorbitol-based clarifying agent on the optical properties and crystallization of LCB-PP under isothermal conditions. The main aims are to provide an overview of the influence of long branches and the nucleating agent on polypropylene during the crystallization process at high crystallization temperatures (T_c).

2. Experimental

2.1. Materials

Two types of commercially available polypropylene grades used for the experiment were obtained from Borealis AG company, Vienna, Austria. Long-chain branched PP was Daploy WB140HMS with melt flow rate (MFR) 2.1 g/10 min, weight-averaged molecular weight of 600 000, and polydispersity index of 5.2. Linear PP was homopolymer Borclean HC300BF with MFR 3.3 g/10 min (both measured at 230 °C, 2.16 kg, ISO 1133), weight-averaged molecular weight of 300 000, and polydispersity index of 8.0. In LCB-PP, long branches were incorporated into the main chain by grafting a monomer by radical means with the help of peroxides. Specific α -nucleating/clarifying agent Millad 3988 (1,3;2,4-bis(3,4-dimethylbenzylidene)sorbitol) [37] supplied by Milliken Chemical Co., (USA) was applied in the concentration of 0.2 wt%.

2.2. Samples preparation

The nucleating agent was mixed into the polypropylenes in two steps, first manually, then using a twin-screw extrusion machine [38]. During the first step, 0.3 wt% of paraffin oil was added to the granulate to improve subsequent dispersion of the nucleating agent Millad 3988 at the concentration of 0.2 wt%. This was followed by mixing using a co-rotating twin screw extruder (Brabender GmbH & Co, Germany) with cooling and pelletizing. The processing conditions during extrusion were set as follows: screw speed 50 min⁻¹, temperatures of barrel zones 180, 200, and 210 °C. To ensure the same processing and thermal history for all samples, neat PP and neat

LCB-PP underwent the same procedure: mixing with paraffin oil and extrusion under the same conditions as those containing nucleating agent.

From the prepared pellets, the plates of a thickness of approx. 0.5 mm were compression-molded: pressing temperature 210 °C for 5 min and cooling temperature 60 °C for 10 min, and polyethylene terephthalate films were used as a separator. Afterward, the specimens were examined by wide-angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC), and optical properties were observed via spectrophotometer. In the following part, nucleated and neat materials are marked as follows: neat linear PP as L-PP, neat long-chain branched PP as LCB-PP, nucleated linear PP as α -L-PP, and nucleated long-chain branched PP as α -LCB-PP.

2.3. Methods

The effect of the α -nucleating/clarifying agent on optical properties was analyzed by haze measurement on as-processed plates using UltraScan Pro D65 instrument, HunterLab, Reston, Virginia, USA, according to ASTM D1003. The measurements were taken five times, and the arithmetic mean was determined. The effect of long branches and the addition of an α -nucleating agent on the crystallization process was studied under isothermal conditions using a differential scanning calorimeter DSC1 (Mettler Toledo, USA). Samples of approx. 5 mg weights were placed in aluminum pans and measured with an empty pan as a reference. Measurements were taken under an inert nitrogen atmosphere with a gas flow of 20 ml/s. The thermal regime was following: heating from 50 to 220 °C by the heating rate of 10 °C/min, annealing at 220 °C for 5 min to remove thermal history, cooling to crystallization temperature (130, 135, 140, 142, 144, 146, 148 and 150 °C) by cooling rate 50 °C/min. Then samples were maintained at crystallization temperature until the crystallization peak was completed, but no longer than 180 min, followed by heating to 190 °C by 10 °C/min to observe the melting profile. The crystalline structure was examined by wide-angle X-ray diffractometer PANalytical X'Pert PRO (Malvern PANalytical, United Kingdom). Diffractometer was equipped with Bragg-Brentano geometry in reflection mode with $\text{CuK}\alpha$ radiation with Ni filter ($\lambda = 0.154$ nm, $I = 30$ mA, $U = 40$ kV) and employed in the diffraction angle interval of $2\theta = 5$ – 30° . Diffractometer was additionally equipped with temperature cell TCU 110 (Anton Paar GmbH, Austria).

Samples were cut to the dimensions 10.0×14.0×0.5 mm to fit in the temperature cell, and the conductive paste was used to ensure good and even thermal conductivity throughout the whole sample. Samples were then heated to 220 °C by 10 °C/min and held at this temperature for 5 min, followed by amorphous halo measurement. After, the samples were cooled to the desired crystallization temperature 140 or 150 °C based on the limit temperatures from DSC measurements by the cooling rate 20 °C/min. At this point, the samples were held at the crystallization temperature for 171 min, and X-ray diffractograms were obtained during the isothermal crystallization process at the given intervals (0, 4, 8, 12, 99, 171 min). The crystallinity of the samples was calculated from the share of the fitted areas of the crystalline part (A_C) and amorphous part (A_A) using Equation (1) [39]:

$$X = \frac{A_C}{A_C + A_A} \cdot 100 [\%] \quad (1)$$

X-ray patterns were analyzed by Scherrer equation (Equation (2)), which gives the length L_{hkl} of the crystallite domain in the direction perpendicular to (hkl):

$$L_{hkl} = \frac{K \cdot \lambda}{FWHM \cdot \cos 2\theta} \quad (2)$$

where λ is the wavelength of the used X-ray, $FWHM$ is the full width at half maximum of the relevant peak, and 2θ is the peak position; both values are in radians. The constant K is omitted by setting it to 1, as in a previous study [39].

3. Results and discussion

3.1. Optical properties

The effectiveness of the nucleating/clarifying agent was examined by measuring the optical properties, namely the haze, of the prepared samples (see Table 1). As can be seen, for L-PP, the addition of the clarifying agent reduced the haze significantly, from 55.0 to 39.7%. Thus, the agent clearly serves its purpose by reducing light scattering, which is a well-known and described effect [25–27]. The haze value of branched polypropylene is very low, even slightly lower than that of α -L-PP (36.5%). This is due to the

Table 1. The haze of the samples.

Sample	L-PP	α -L-PP	LCB-PP	α -LCB-PP
Haze [%]	55.0±0.4	39.7±0.3	36.5±0.3	32.1±0.4

self-nucleation effect of LCB-PP, where the crystallites cannot grow to larger sizes leading to a reduced haze [2–4, 22]. This self-nucleation appears to be more efficient in terms of optical properties than the used clarifying agent Millad 3988. The addition of this agent to the LCB-PP leads to a further slight haze reduction to a value of 32.1%. Although the change is not dramatic, the clarifying agent performs its function even in branched polypropylene.

3.2. Thermal behavior

Using DSC, the effect of long branches and nucleating agent on crystallization was observed under isothermal crystallization conditions. Crystallization temperature varied from 130 to 150 °C, and crystallization time was not longer than 180 min. In the case of linear polypropylene, the crystallization was completed only at 130 and 135 °C in the given time frame. On the other hand, at these temperatures, the crystallization exotherms of LCB-PP and both nucleated polypropylenes were not possible to examine due to continuous crystallization even during cooling to crystallization temperature; thus, the exotherms were not complete. Figure 1 shows the sigmoidal crystallization curves of samples isothermally crystallized at temperatures 140, 142, 144, 146, 148 and 150 °C. Only the samples where whole crystallization exotherms were obtained are shown. Figure 2 depicts the correlation between the crystallization half-time and the crystallization temperature across all samples, obtained from the sigmoidal curves from Figure 1. It is evident that the addition of an α -nucleating agent significantly accelerates the crystallization of linear PP. On the contrary, neat LCB-PP behaves as if it already contains heterogeneous nucleation seeds. These heterogeneous nucleation seeds could be local cross-linking formed during the production of branched polypropylene. LCB-PP used in this study was produced by a radical mechanism with the help of peroxides, and during this process, in addition to branching, a gel may also be formed, or even chain splitting can occur [40]. This heterogeneous self-nucleation significantly influences crystallization, and the addition of nucleating agents does not significantly affect the kinetics of crystallization. Indeed, crystallization curves of branched polypropylenes with/without a nucleating agent are very similar, especially at higher crystallization temperatures. The slight acceleration of crystallization after the addition of the nucleating agent is clearly

visible only at a crystallization temperature of 140 °C. This observation may be related to the minor improvement in the optical properties of LCB-PP after the addition of the agent used. The crystallization curve of nucleated linear PP is always shifted to higher times compared to those of branched PP, and the difference is more significant the higher the crystallization temperature. Moreover, at higher temperatures, the curve is deformed (144 and 146 °C), and at temperatures of 148 and 150 °C, the crystallization was not complete in the given time of 180 min. The curves are, therefore, not shown. Evidently, the nucleating agent loses its nucleating capability at such high temperatures. The above-mentioned deformation of the α -L-PP crystallization curves is due to the formation of asymmetric crystallization exotherms that exhibited shoulder or doubling (Figure 3). This phenomenon is probably caused by two crystallization mechanisms occurring simultaneously. At such high temperatures, the nucleating agent that dissolves in the PP melt apparently crystallizes only to a limited extent, and its function fails [37].

The crystallization half-time of LCB-PP with and without a nucleating agent follows a similar pattern, with differences only apparent at high crystallization temperatures of 148 and 150 °C, where the presence of the nucleating agent decelerates the crystallization process (Figure 2). This is likely due to the nucleating agent not being able to fully crystallize at these high temperatures and potentially diluting the PP melt [37]. The nucleating agent only slightly accelerates the crystallization of LCB-PP at a crystallization temperature of 140 °C. Evidently, the effect of the nucleating agent used depends on the thermal regime applied. Notably, neat LCB-PP was found to crystallize faster than α -L-PP. Thus, the effect of self-nucleation in LCB-PP is more pronounced than the addition of the α -nucleating agent to L-PP.

The isothermally crystallized samples were then heated to determine the melting temperature (melting temperature is the peak of the endotherm). The results are shown in Figure 4. A correlation between the increase in crystallization temperature and the increase in melting temperature is observed. In the case of neat L-PP, the full crystallization was achieved only at temperatures of 130 and 135 °C, and thus only these samples were melted. The melting behavior of such material shows the presence of both α - and β -phases with melting temperatures approx. 155 and 167 °C, respectively, in the case of lower crystallization

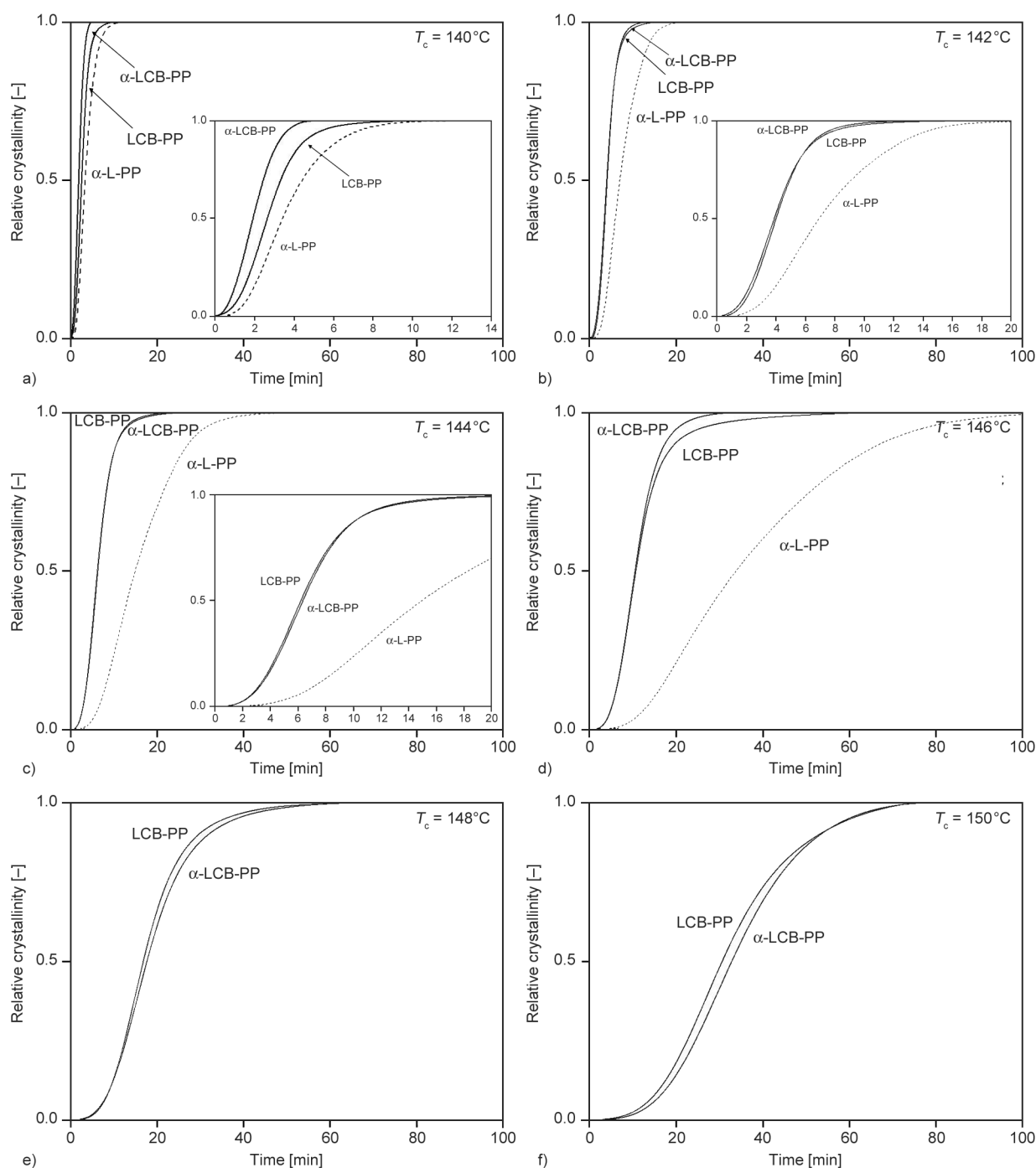


Figure 1. Crystallization curves of isothermally crystallized samples at various crystallization temperatures (the inset shows an x-axis cutout), a) $T_c = 140^\circ\text{C}$, b) $T_c = 142^\circ\text{C}$, c) $T_c = 144^\circ\text{C}$, d) $T_c = 146^\circ\text{C}$, e) $T_c = 148^\circ\text{C}$, f) $T_c = 150^\circ\text{C}$.

temperature. It should be noted that the melting peak of the β -phase was significantly smaller compared to that of the α -phase, corresponding to the very low content of β -phase in the sample (this will be proved thereafter by X-ray analysis). On the contrary, when adding an α -nucleating agent, no melting endotherm of β -phase was observed. Two values of melting point in the case of samples crystallized at high temperatures 144 and 146°C refer to the presence of α_1 (at approx. 170°C) and α_2 (at approx.

174°C) phases [41, 42]. All LCB-PP samples show only one endotherm corresponding to the melting of α -phase, and, moreover, the values are very similar independently of the presence of the nucleating agent. Compared to linear polypropylene, the melting temperatures of LCB-PP samples are significantly lower, approx. 162 vs. 167°C for a crystallization temperature of 140°C . This suggests that the formation of thinner lamellae is associated with the presence of branching in polypropylene.

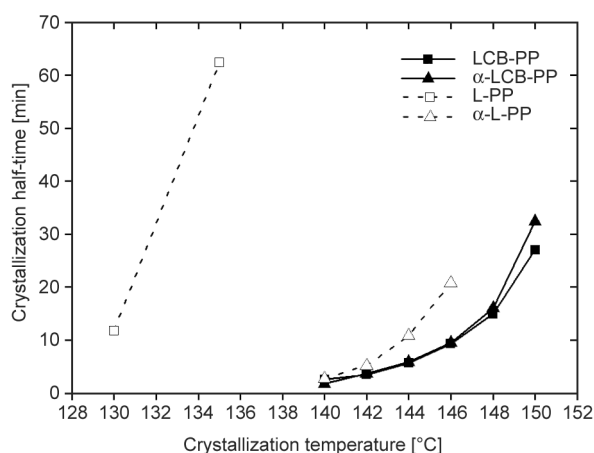


Figure 2. Crystallization half-time of samples crystallized at various crystallization temperatures.

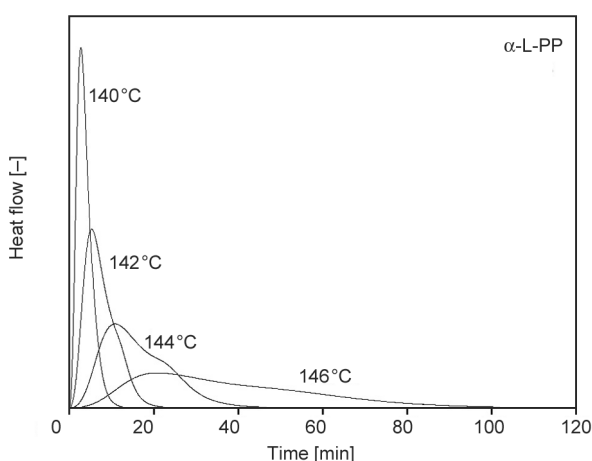


Figure 3. Crystallization exotherms of α -L-PP at various crystallization temperatures.

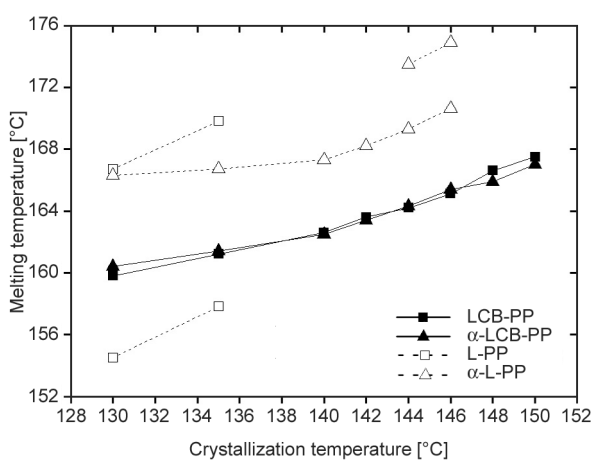


Figure 4. Melting temperatures of samples crystallized at various crystallization temperatures.

3.3. Supermolecular structure

Wide-angle X-ray scattering (WAXS) equipped with a temperature cell was used to study the morphology of isothermally crystallized samples. The crystallization temperatures 140 and 150 °C were chosen as

representatives based on the results from thermal analysis. The measurement took place after melting the sample, then after reaching the crystallization temperature, and during crystallization at specified intervals. It is worth mentioning that the thermal conditions in the sample were different for WAXS than for DSC due to the different sizes of the sample, the atmosphere during the measurement, and mainly the cooling rate. Therefore, the results are not entirely comparable to the results from the DSC.

The presence of peaks corresponding to the main planes of the α -phase $\alpha(110)$, $\alpha(040)$, and $\alpha(130)$, β -phase (300) and γ -phase (117) can be observed in the typical diffraction spectra of three-phase crystalline systems [22]. X-ray diffractograms of all polypropylene samples, see Figure 5, show the evolution of phases during isothermal crystallization at selected times. The initiation of the crystallization process in neat L-PP isothermally crystallized at 140 °C occurred at crystallization time (t_c) 8 min of time-dependent crystallization. The final pattern (after t_c 171 min at 140 °C) contains, in addition to the α -diffraction peaks at angles $2\theta = 14.20$, 17.00 and 18.80° , a small diffraction peak associated with the presence of the β -phase (16.20°) and also a small broad γ -phase diffraction peak (20.05°). Thus, a three-phase system with a dominant amount of α -phase was formed. Adding of a nucleating agent to the linear polypropylene significantly accelerated the crystallization process, which proceeded even upon cooling to a crystallization temperature of 140 °C. Moreover, the formation of the β -phase was suppressed entirely, while the diffraction peak corresponding to the γ -phase was observed. Thus, a two-phase α/γ system with α -phase dominance was formed. Increasing the crystallization temperature to 150 °C leads to a retardation of crystallization in both cases, with/without the nucleating agent, and also to the exclusive formation of the α -phase: no β - and γ -diffraction peaks were observed. Indeed, these phases cannot be formed at such a high temperature [43].

Diffraction patterns of LCB-PP crystallized at 140 and 150 °C are also shown in Figure 5. Since the patterns of nucleated LCB-PP were the same as those of neat LCB-PP, they are not shown in the figure. LCB-PP crystallized into both the α - and γ -phases at 140 °C. At 150 °C, the crystallization was slightly slower, and the γ -phase diffraction peak disappeared.

From the crystallization patterns, crystallinity was calculated and plotted as a function of time in Figure 6.

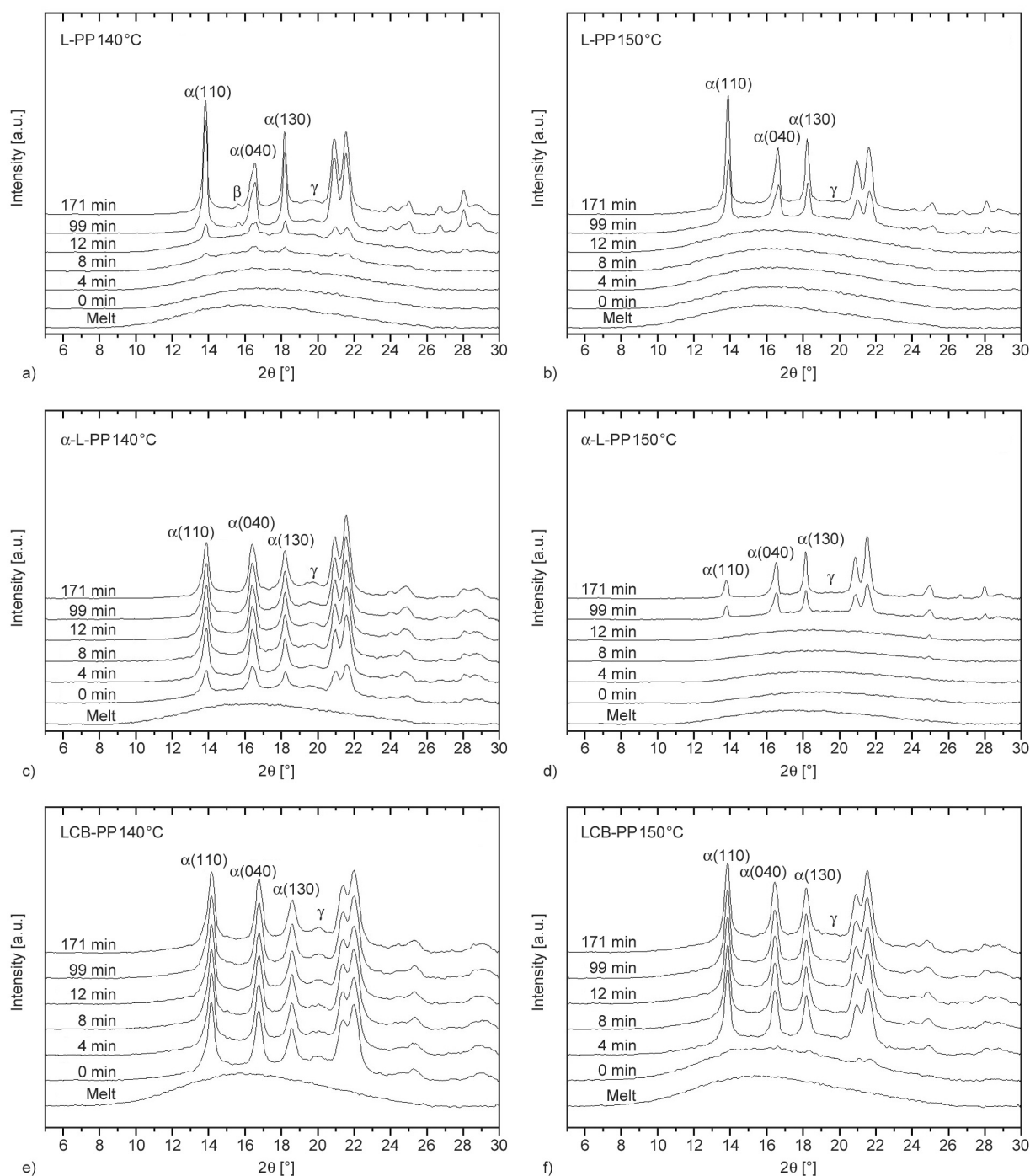


Figure 5. WAXS patterns of neat and nucleated linear polypropylene and neat long-chain branched polypropylene crystallized at 140 and 150 °C, a) L-PP at 140 °C, b) L-PP at 150 °C, c) α -L-PP at 140 °C, d) α -L-PP at 150 °C, e) LCB-PP at 140 °C, f) LCB-PP at 150 °C.

In the case of crystallization at 140 °C, except for L-PP, all samples crystallized upon cooling to the crystallization temperature. Both LCB-PP samples crystallize faster than α -L-PP due to their ability to self-nucleate, which is consistent with the DSC measurement results. The achieved crystallinity is higher for linear PP than for LCB-PP. Adding a nucleating agent leads to a slight decrease in crystallinity

in the case of L-PP. However, no effect is observed in the case of LCB-PP. At a higher crystallization temperature of 150 °C, the addition of a nucleating agent to LCB-PP leads to a very slight acceleration of crystallization and also to a slightly higher crystallinity. Linear polypropylene crystallizes reluctantly at this high temperature, and adding the nucleating agent leads to acceleration, but not significantly. In

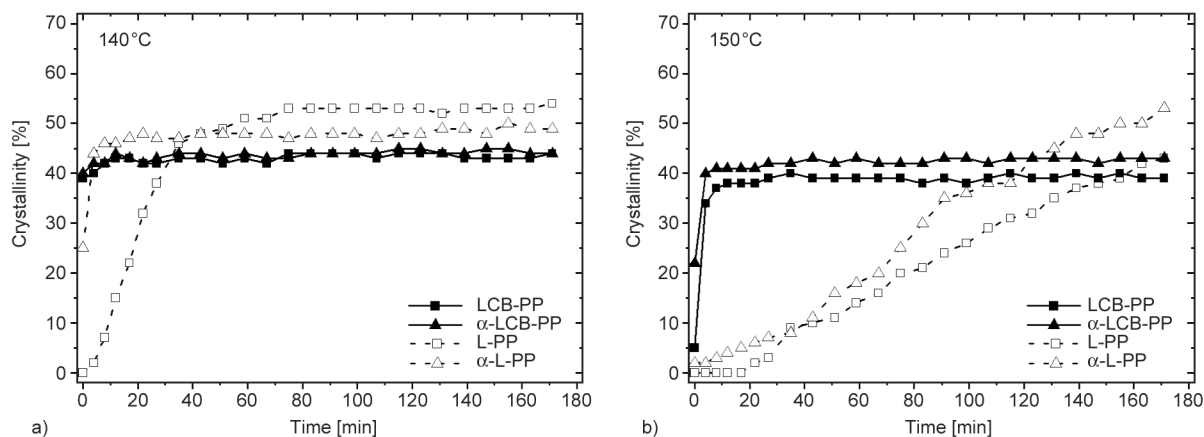


Figure 6. Evolution of overall crystallinity during time-dependent isothermal crystallization at a) 140 °C and b) 150 °C.

the time taken for isothermal crystallization, the plateau was not reached, so the final crystallinity values could not be evaluated, but they are certainly higher than in the case of LCB-PP. Although it is impossible to fully compare these results with those from the DSC due to the different analysis conditions, the trends are the same, and the results confirm and complement each other.

From the diffractograms obtained at the longest crystallization time, *i.e.*, 171 min, the values of the lamellae length in the (110), (040), and (130) directions of the α -crystallites were calculated (Table 2). In the case of linear PP crystallized at 140 °C, the addition of the nucleating agent leads to a significant reduction in lamellae length. However, for a crystallization temperature of 150 °C, this is not the case; the length of the lamellae remains the same independently of the addition of the nucleating agent; thus, at this high temperature, it does not fulfill its function. The length of the lamellae of branched polypropylene crystallized at 140 °C is even shorter than in the case of linear with the nucleating agent, and the addition of the agent leads to a further slight decrease, indicating its efficiency. This is in good agreement with haze measurement. However, the same trend is observed at the higher crystallization temperature of 150 °C: the addition of the nucleating agent also

leads to a reduction in lamellae length. Thus, the molecular structure of polypropylene seems to influence the efficiency of the nucleating agent.

4. Conclusions

This study shows the combined effect of long-chain branches and the addition of commercial sorbitol-based α -nucleating/clarifying agent Millad 3988 on the optical properties, crystallization, and supermolecular structure of polypropylene. As expected, adding this nucleating agent significantly reduces the haze of common linear polypropylene. In the case of LCB-PP, which itself shows lower haze than L-PP with the nucleating agent, a slight reduction is also observed.

Used nucleating agent selectively affects polymorphic phases, suppresses β -phase growth, and slightly decreases crystallinity in L-PP. Moreover, it significantly speeds up the crystallization at lower crystallization temperatures up to 146 °C while affecting the mechanism of crystallization, forming double exotherms, especially at higher crystallization temperatures. For LCB-PP, it was found that polymorphic composition does not depend on the addition of the nucleating agent; however, the crystallinity slightly increases. Also, the crystallization rate is not considerably affected by the addition of nucleating agent into LCB-PP, which is nevertheless higher than that of nucleated linear polypropylene. Only a slight positive effect is observed at the lowest crystallization temperature and a negative effect at higher crystallization temperatures. LCB-PP favors self-nucleation due to long branches acting as defects in structure and, thus, as heterogeneous nucleation seeds.

To conclude, although the used nucleating/clarifying agent appears to have a slight effect on the optical

Table 2. Lamellae length calculated from WAXS data.

Material	140 °C			150 °C		
	L_{110} [nm]	L_{040} [nm]	L_{130} [nm]	L_{110} [nm]	L_{040} [nm]	L_{130} [nm]
L-PP	42.8	19.0	42.6	42.8	42.7	42.6
α -L-PP	34.3	21.4	34.1	42.8	42.7	42.6
LCB-PP	28.5	24.4	21.3	34.3	28.5	28.4
α -LCB-PP	24.5	19.0	18.9	28.5	24.4	24.3

properties of long-chain branched polypropylene, it does not affect the crystallization kinetics significantly.

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